

Soybean Oil-Based Lubricants: A Search for Synergistic Antioxidants[†]

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Vegetable oils can contribute toward the goal of energy independence and security due to their naturally renewable resource. They are promising candidates as base fluids for ecofriendly lubricants because of their excellent lubricity, biodegradability, good viscosity–temperature characteristics, and low evaporation loss. Their use, however, is restricted due to low thermo-oxidative stability and poor cold-flow behavior. This paper presents a systematic approach to improve their oxidation behavior by searching for a suitable additive combination. The study of antioxidant/antiwear additive synergism was investigated on a set of four antioxidants and three antiwear additives in vegetable oils using pressure differential scanning calorimetry (PDSC) and a rotary bomb oxidation test (RBOT). The results indicate that dialkyldithiocarbamate antioxidant performed better than diphenylamine and hindered phenol. The zinc dialkyldithiocarbamate antioxidant showed excellent synergism with antiwear additive antimony dithiocarbamates.

Introduction

A significant lubricant market of about 2.4 billion gallons per year of industrial and automotive lubricants exists.²⁹ Lubricants account for 1.2% of total petroleum use, and vegetable oils provide only about 0.1% of the lubricant market. Due to strict environmental regulations and a concern for depletion of world fossil fuel reserves, there has been a constantly increasing demand for biobased lubricants in applications like total loss lubrication, military, railroads, and outdoor activities such as forestry, mining, dredging, fishing, and agriculture hydraulic systems.¹

Vegetable oil-based lubricants are biodegradable and non-toxic, unlike conventional mineral oil-based ones.^{2,3} They have low volatility due to the high molecular weight of the triglyceride molecule and a narrow range of viscosity change with temperature. Polar ester groups are able to adhere to metal surfaces and, therefore, possess good boundary lubrication properties. In addition, polar contaminants and additive molecules are highly soluble in vegetable oils.

One of the drawbacks of vegetable oils is their poor oxidative stability.^{4,5} This is primarily due to the presence of bis-allylic protons, which are highly susceptible to radical attack and subsequently undergo oxidative degradation to form polar oxy-

compounds. This phenomenon results in insoluble deposits and increases oil acidity and viscosity. Oxidation is the single most important reaction of oils resulting in increased acidity, corrosion, viscosity, and volatility when used as lubricant base oils.

The oxidative stability of lubricating oils and the oxidation inhibition capacity of antioxidant additives can be evaluated using various methods such as pressurized differential scanning calorimetry (PDSC), rotary bomb oxidation test (RBOT), thin film micro-oxidation test (TFMO), turbine oil stability test (TOST), and hydroperoxide titration test. RBOT is a rapid method and has been used to study the oxidation stability of lubricating oils by many workers.^{6–8} Recent studies have shown that PDSC is an effective way to evaluate the antioxidant efficiency and oxidation stability of base oils.^{9–11} The use of high pressure for PDSC inhibits the volatilization loss of lubricants and saturates the liquid phase with oxygen, which results in an acceleration of oxidation as well as a sharpening of the lubricant exotherm compared with normal DSC. This allows the use of lower test temperatures or shorter test times at the same temperatures. PDSC is also a rapid and accurate technique for measuring parameters that correlate with the oxidation reaction of oils.^{9,12,13} PDSC experiments are run either in an isothermal mode to measure oxidation induction time^{1,8,9}

[†] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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(1) Rhee, I. *NLGI Spokesman* **1996**, 60 (5), 28–34.

(2) Randles, S. J.; Wright, M. J. *Synth. Lubr.* **1992**, 9, 145–161.

(3) Battersby, N. S.; Pack, S. E.; Watkinson, R. J. *Chemosphere* **1998**, 24, 1998–2000.

(4) Gapinski, R. E.; Joseph, I. E.; Layzell, B. D. *SAE Tech. Pap.* **1994**, 941785, 1–9.

(5) Becker, R.; Knorr, A. *Lubr. Sci.* **1996**, 8, 95–117.

(6) Cermak, S. C.; Isbell, T. A. *Ind. Crop Prod.* **2003**, 18 (3), 223–230.

(7) Gatto, V. J.; Grina, M. A.; Tat, T. L.; Ryan, H. T. *J. Synth. Lubr.* **2002**, 19 (1), 3–18.

(8) Qiu, C.; Han, S.; Cheng, X.; Ren, T. *Thermochim. Acta* **2006**, 447, 36–40.

(9) Sharma, B. K.; Stipanovic, A. J. *Thermochim. Acta* **2003**, 402 (1–2), 1–18.

(10) Sharma, B. K.; Adhvaryu, A.; Sahoo, S. K.; Stipanovic, A. J.; Erhan, S. Z. *Energy Fuels* **2004**, 18 (4), 952–959.

(11) Adhvaryu, A.; Sharma, B. K.; Hwang, H. S.; Erhan, S. Z.; Perez, J. M. *Ind. Eng. Chem. Res.* **2006**, 45, 928–933.

(12) Kowlaski, B.; Gruczynska, E.; Maciaszek, K. *Eur. J. Lipid Sci. Technol.* **2000**, 102 (5), 337–341.

(13) Adhvaryu, A.; Erhan, S. Z.; Liu, Z. S.; Perez, J. M. *Thermochim. Acta* **2000**, 364, 87–97.

or a programmed temperature mode to measure the onset temperature^{10,11,13,14} of lubricant oxidation.

This paper reports the enhanced ability of additive combinations to resist oxidative deterioration at elevated temperatures to extend the applicability of vegetable oil-based lubricants. The effectiveness of three different classes of antioxidants was investigated using the RBOT and both programmed temperature and isothermal PDSC. Additionally, the synergistic effects of suitable combinations of antioxidants with antiwear additives and the impact of lowered multiple unsaturation on additive response were examined.

Experimental Section

Materials. The soybean oil (SO) used in this study was alkali refined (ADM Packaged Oils, Decatur, IL) and used without any further purification. The antioxidant additives used were alkylated diphenylamine (ADPA), butylated hydroxy toluene (BHT), a mixture of alkylated phenol/dithiophosphoric acid ester/diphenylamine (APDD), and zinc diamyl dithiocarbamate (ZDDC). The antiwear additives included antimony dialkyldithiocarbamate (ADDC), an amine-phosphate compound (AP), and molybdenum dialkylphosphorodithioate (MDPD). All these antioxidant and antiwear additives were obtained from RT Vanderbilt Co (Norwalk, CT), except APDD which was obtained from Lubrizol Corp. (Wickliffe, OH).

Programmed Temperature PDSC. The experiments were conducted using a DSC 2910 thermal analyzer from TA Instruments (New Castle, DE) attached to a computer. Typically, a 2 μ L sample was placed in a hermetically sealed type aluminum pan with a pinhole lid for interaction of the sample with the reactant gas (dry air). A film thickness of less than 1 mm was required to ensure proper oil-air interaction and to eliminate gas diffusion limitations. The module was temperature calibrated using the melting point of indium metal (156.6 °C) at a 10 °C/min heating rate. Dry air (Gateway Airgas, St. Louis, MO) was pressurized in the module at a constant pressure of 1379 kPa (200 psi) with no flow. A constant scanning rate of 10 °C/min was used for the temperature ramping experiments. The oxidation onset temperature (OT) and signal maxima temperatures (SM) of oxidation were calculated from the exotherm in each case. The OT is the temperature at which a rapid increase in the rate of oxidation is observed and is obtained by extrapolating the tangent drawn on the steepest slope of reaction exotherm. A higher OT would suggest a higher oxidation stability of the oil. All oil samples were run in triplicate and the average OT and SM were reported with a standard deviation of <1.0.

Isothermal PDSC in Dynamic Air Pressure. The synergistic response of additive combinations in soybean oil was also studied using isothermal PDSC. These experiments were performed on 2 μ L oil samples in sealed aluminum hermetic pinhole pans under 1379 kPa (200 psi) of high-purity dry air. These conditions maintain maximum contact between air and the sample and eliminate any limitations due to oxygen diffusion in the oil medium. Air flow was maintained at 34 ± 5 mL/min. Oil samples containing additive combinations were heated from ambient temperature to 140 or 170 °C at a heating rate of 40 °C/min before being held in an isothermal mode until an exothermic peak of oxidation appeared. Oxidation induction time (OIT) was measured from the time isothermal conditions were achieved to the start of the exothermic peak. All oil samples were run in triplicate, and the average oxidation induction times were reported.

Oxidation Stability Using RBOT. Rotary bomb oxidation tests of all the oil formulations were carried out as per ASTM D 2272. The method uses 50 g of oil in the presence of copper catalyst at 150 °C under dry conditions. In RBOT, the vessel was charged with oxygen to 620.5 kPa (90 psi) pressure and rotated axially in a constant temperature oil bath set at 150 °C. The pressure in the bomb was recorded with time, and the RBOT time is the time at

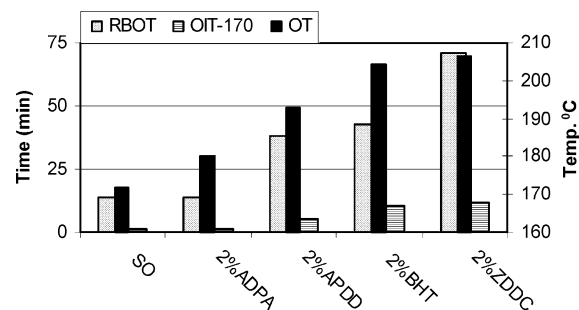


Figure 1. Comparison of selected antioxidants in soybean oil using programmed temperature (PT) PDSC, isothermal PDSC (170 °C), and RBOT.

which the maximum pressure of the bomb has dropped by 175.1 kPa (25.4 psi). The RBOT time usually coincides with an induction-type period. The rapid pressure drop is due to consumption of higher amounts of oxygen as a result of depletion of the antioxidant and corresponds to the time when the rate of oxidation of lubricant in the bomb is at its maximum. In this test, soybean oil without any antioxidant has a RBOT time of 14 min. All oil samples were run in duplicate, and the average RBOT times were reported. Agreement between RBOT test times was <2 min for all tests.

Results and Discussion

Two PDSC methods and a RBOT method were used to study the antioxidant effects of individual antioxidants and various additive combinations in soybean oil.

Comparison of Antioxidant Response in Oxidation Tests.

Figure 1 shows the results of the PDSC temperature ramping experiment, PDSC isothermal method, and RBOT for the selected antioxidants in soybean oil. The OT obtained from PDSC temperature ramping experiments varies from 171 °C for SO to 207 °C for 2% ZDDC in soybean oil. The OIT of the soybean oil samples containing additives were obtained from PDSC isothermal experiment at 170 °C. At 170 °C, ZDDC exhibited the highest OIT value of 12 min followed by 11 min for BHT and 5 min for APDD, while ADPA had a value similar to that of neat soybean oil. It is very difficult to choose a suitable isothermal condition for measuring the OIT of all oil samples in the matrix. Different isothermal temperatures may be required to generate a repeatable OIT. The RBOT time of neat soybean oil and ADPA is 14 min, while it is highest for ZDDC (71 min) followed by 43 min for BHT and 38 min for APDD.

All three oxidation tests, isothermal PDSC, programmed temperature PDSC, and the RBOT, provided a similar ranking of the additives, showing good correlation between PDSC and RBOT techniques. Figure 1 shows that zinc diamyl dithiocarbamate (ZDDC) has good antioxidant activity and the performance of butylated hydroxyl toluene (BHT) is better than the mixture of alkylated phenol/dithiophosphoric acid ester/diphenylamine (APDD). The alkylated diphenylamine (ADPA) exhibited the poorest performance. The antioxidant capacity of ADPA appears to be inhibited in these experimental conditions, when compared to untreated soybean oil. This is unexpected as hindered phenols and diphenylamines are predicted to follow the basic radical scavenging mechanism. The diphenylamines exhibit good antioxidant properties at higher temperatures (above 175 °C) and have been reported to exhibit radical scavenging activity by N-H abstractions as well as via their corresponding nitrosyl radicals in petroleum-based oils.¹⁵⁻¹⁸ The poor perfor-

(15) Gatto, V. J.; Grina, M. A. *Lubr. Eng.* **1999**, 55 (1), 11-20.

(16) Hunter, M.; Klaus, E. E.; Duda, J. L. *Lubr. Eng.* **1993**, 49, 492-498.

(14) Dunn, R. O. *Trans. ASAE* **2000**, 43 (5), 1203-1208.

mance of ADPA may be ascribed to the low temperatures (150 °C) used in this study as diphenylamines follow different inhibition mechanisms at low and high temperatures. This observation has been confirmed by another study also, where diphenylamines performed poorer in vegetable oils at an oxidation test temperature of 130 °C.⁵ The APDD additive mix was less effective than BHT, implying further that the diphenylamine present in APDD was a less effective antioxidant than BHT itself in vegetable oils. The hindered phenolic group present in BHT also functions as a radical scavenger. Under RBOT oxidation conditions in vegetable oils, hindered phenols regenerate and scavenge peroxy radicals stoichiometrically while diphenylamines appear not to scavenge peroxy radicals. This observation is in contrast to previously reported works,^{19–21} where it has been shown that ADPA scavenges radicals catalytically under high oxygen concentrations and temperatures above 175 °C while phenolic groups scavenge radicals on a stoichiometric basis. This suggests that the mechanism of radical scavenging for hindered phenols and diphenylamine is different under these oxidation conditions and also differs in vegetable oils compared to mineral-based oils.

The antioxidant ZDDC performed better than diphenylamine and hindered phenol in vegetable oils, and this observation has been supported by previous studies.⁵ ZDDC functions both as radical scavenger and hydroperoxide decomposer that reduces the hydroperoxides formed during the oxidation process to nonradical products like alcohols while being oxidized in a sacrificial manner, thus preventing chain propagation. Upon closer inspection, the data shows that ZDDC and BHT have identical responses by the PDSC test methods and that the only distinction in antioxidant performance is seen by the RBOT method. The property of ZDDC that makes it perform better than BHT in the RBOT is its corrosion-inhibiting/metal-deactivating property. This property of ZDDC may be responsible for its ability to inhibit the copper catalyst that is a part of the RBOT method. Metal deactivators are strong metal ion complexing agents that inhibit catalyzed reactions by chelation, thus showing an antioxidant effect. It is thus possible that, if a suitable metal deactivator such as tolutriazole or a derivative is used for RBOT evaluations of BHT and ADPA, these additives may also show an enhanced antioxidant effect.

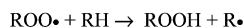
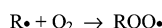
The current accepted theory of the role of antioxidants as radical scavengers or hydroperoxide decomposers can be explained as oxidation taking place through a radical-initiated chain mechanism involving: initiation, propagation, branching, chain inhibition, and peroxide decomposition as shown in Scheme 1. In the case of vegetable oils, the RH represents an unsaturated fatty acid arm of triacylglycerol with H attached to an allylic carbon atom. At high temperatures, thermal initiation is possible to give rise to free radicals in the first step. The free radicals thus generated react with oxygen to form peroxy free radicals and hydroperoxides in the chain propagation step. During this period, oxygen is consumed in a zero-order process, apparently leading to intermediates that are not too well characterized, prior to the formation of peroxides. The latter undergoes further reaction to form alcohols, ketones, aldehydes,

Scheme 1. Oxidation Mechanism in Oils

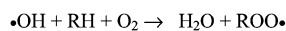
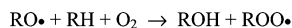
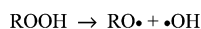
Chain initiation



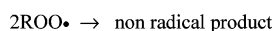
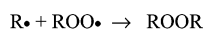
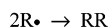
Chain propagation



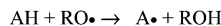
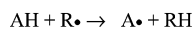
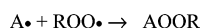
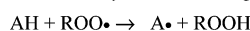
Chain branching



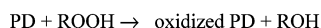
Chain termination



Inhibition by radical scavengers (AH)



Oxidation inhibition by peroxide decomposers (PD)



and carboxylic acids, leading to rancidity and toxicity, thereby accelerating the oil degradation process. These compounds have molecular weights that are similar to vegetable oils and therefore remain in solution. As the oxidation proceeds, the oxygenated compounds polymerize to form viscous material that, at a particular point, becomes oil insoluble leading to oil thickening and deposits.

The presence of unsaturation in the triacylglycerol molecule due to C=C from oleic, linoleic, and linolenic acid moieties functions as the active sites for radical initiated oxidation reactions. Saturated fatty acids are less prone to this radical initiated oxidation and thus have high oxidation stability. The structure of radical R• thus influences the rate of reaction. The oxidation rate of linolenate is 77 times faster than that of oleate, while that of linoleate is 27 times faster compared with that of oleate.²² This sequence of reactions is affected by pro-oxidants like metals and antioxidants (AH shown in scheme) with the latter improving oxidation stability. An antioxidant like ZDDC acting as a peroxide decomposer and metal deactivators inhibits the chain initiation step of oxidation, thus preventing the formation of free radicals and hydroperoxides. Antioxidants BHT and ADPA acting as radical scavengers inhibit the chain propagation step. It appears that the best way to control oxidation in vegetable oils under these conditions is by using an antioxidant that inhibits the chain initiation step rather than the chain propagation step of oxidation.

Response of Antioxidant ADPA in the Presence of Antiwear Additives. The tribological behavior of antiwear additives ADDC, AP, and MDPD have been well studied in the past.²³

(22) Gunstone, F. D. Chemical Properties. In *The Lipid Handbook*, 2nd ed.; Gunstone, F. D., Harwood, J. L., Padley, F. B., Eds.; Chapman & Hall: New York, 1984; pp 566–571.

(23) Sarin, R.; Tuli, D. K.; Sureshbabu, A. V.; Misra, A. K.; Rai, M. M.; Bhatnagar, A. K. *Tribol. Int.* **1994**, 27 (6), 379–86.

(17) Denisov, E. T.; Khudyakov, I. V. *Chem. Rev.* **1987**, 87, 1313–1357.

(18) Kozakowaski, G.; Kolodziejewski, W. *J. Synth. Lubr.* **1990**, 7, 229–241.

(19) Thomas, J. R.; Tolman, C. A. *J. Am. Chem. Soc.* **1962**, 84 (15), 2930–2935.

(20) Thomas, J. R. *J. Am. Chem. Soc.* **1960**, 82 (22), 5955–5956.

(21) Korcek, S.; Jensen, R. K.; Zinbo, M.; Gerlock, J. L. In *Organic Free Radicals*; Fischer, H., Weingarten, H., Eds.; Springer-Verlag: Berlin, 1988; pp 95ff.

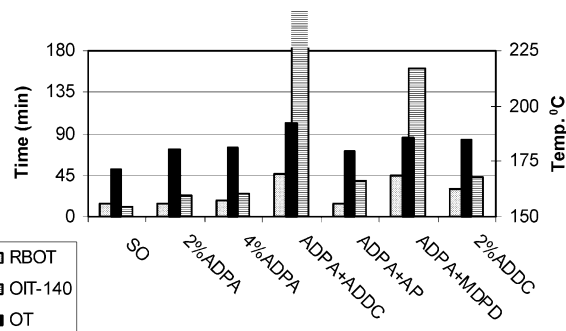


Figure 2. ADPA antioxidant response in combination with antiwear additives using PT PDSC, isothermal PDSC (140 °C), and RBOT.

However, it is important to understand how these antiwear additives affect the antioxidant efficiency of different additives in multicomponent systems. The effects of antiwear additives, ADDC, AP, and MDPD on the effectiveness of antioxidants, ADPA, BHT, APDD, and ZDDC, in soybean oil were evaluated in the isothermal PDSC, programmed temperature PDSC, and RBOT methods.

Figure 2 summarizes results obtained with combinations of antioxidant ADPA and antiwear additives (ADDC, AP, and MDPD) in soybean oil. Very little improvement in onset temperature, oxidation induction time, and RBOT time was found by increasing the concentration of antioxidant ADPA from 2% to 4%. On addition of 2% antiwear additives to 2% ADPA in soybean oil, there was some improvement, except for AP. The addition of ADDC to diphenylamine improved the inhibition compared to other two additives evaluated. Tests for SO and 2% ADDC in SO are shown for comparative purposes.

The addition of 2% MDPD to 2% ADPA in soybean oil did increase the OT, OIT, and RBOT time. Both ADDC and MDPD enhanced the performance of antioxidant ADPA while AP made no difference in the antioxidant efficiency of ADPA. Isothermal PDSC results showed a 10-fold increase in OIT on adding ADDC and a 5-fold increase with MDPD when compared to 2% ADPA antioxidant by itself. RBOT times increased 2-fold on addition of ADDC and MDPD to 2% ADPA solution in soybean oil. This difference in activity is probably due to the lower isothermal temperature used in PDSC compared to RBOT and differences in their test conditions. The improved antioxidant performance of ADPA in the presence of antiwear additives ADDC and MDPD relative to amine-phosphate suggests that sulfur in these two antiwear additives contributed to antioxidant efficiency in these tests. The activities of dithiocarbamate and phosphorodithioate as hydroperoxide decomposers along with the radical scavenging nature of diphenylamine provided improved protection in these combinations.

Response of Antioxidant BHT in Combination with Antiwear Additives. Figure 3 shows the results of the concentration effects and its combinations with antiwear additives. As the concentration of BHT is increased from 1% to 4%, there is an increase in RBOT time and onset temperature at 2% and a slight increase to 3% but essentially no change at 4%. At higher concentrations, the stabilizing effect per mole-equivalent inhibitor decreased remarkably. The oxidation induction time determined using isothermal PDSC at 170 °C showed a similar concentration effect. Perhaps under the high temperature and pressure conditions of the PDSC isothermal test, phenolic peroxide intermediates decompose. This requires a constant supply of hindered phenols in the system, thus showing a linear concentration dependence under these conditions.

Except for additives ADDC and ZDDC, the addition of other antiwear additives to 2% BHT in soybean oil results in

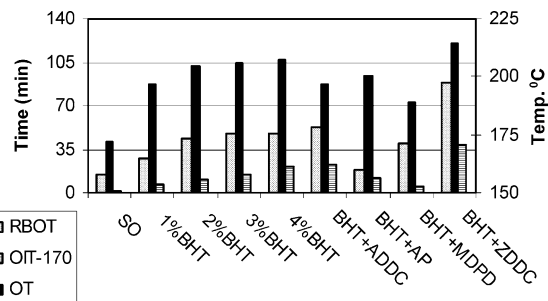


Figure 3. Antioxidant response of additive BHT in combination with antiwear additives using PT PDSC, isothermal PDSC (170 °C), and RBOT.

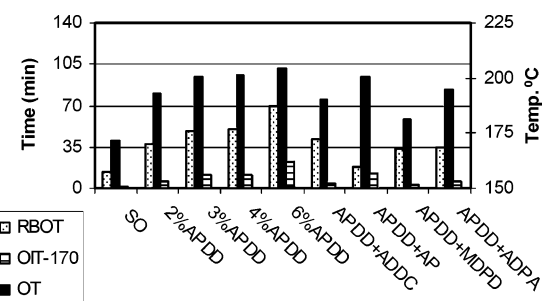


Figure 4. Antioxidant response of additive APDD in combination with antiwear additives using PT PDSC, isothermal PDSC (170 °C), and RBOT.

essentially no improvement or an antagonistic effect on oxidation stability. The ADDC almost doubled the OIT of the phenolic additive in soybean oil, while the RBOT time has been increased by 25%. The presence of the other two antiwear additives AP and MDPD in multicomponent systems decreased the antioxidant efficiency of the phenolic antioxidant. It appears that, in this system, the AP and MDPD antiwear additives are acting as pro-oxidants by generating more radicals that propagate oxidation. The addition of another multifunctional additive ZDDC to the phenolic additive system increased the antioxidant efficiency to a much greater extent, even more than that of ADDC. This further confirms the possibility that addition of metal deactivators to BHT and ADPA solutions may improve the performance in RBOT test just as addition of ZDDC (which acts as metal deactivator) increased the antioxidant efficiency of BHT.

Response of Antioxidant APDD in Combination with Antiwear Additives. Figure 4 shows the results of the concentration effects of antioxidant APDD and when it is used with antiwear additives. APDD is a mixture of additives containing a most commonly used combination of hindered phenols/diphenylamine along with dithiophosphoric acid ester. This combination performs well in petroleum-based oils. A phenolic to diphenylamine ratio of 1:1 was reported to provide the best antioxidant effect in petroleum-based oils.¹⁵ A linear relationship has been observed for APDD concentrations up to 6% for RBOT time, oxidation induction time obtained at an isothermal temperature of 170 °C, and PDSC onset temperatures. This complies with the findings for a 1:1 phenolic/diphenylamine combination in petroleum-based oil using a concentration range up to only 0.5%.¹⁵

Interesting results were obtained when 2% antiwear additives were added to 2% solutions of APDD in soybean oil. In the PDSC results, addition of AP to APDD in soybean oil showed slight improvement. ADDC, which showed synergism with the other two antioxidants ADPA and BHT, showed no effect, while MDPD showed a pro-oxidant effect with APDD in soybean oil.

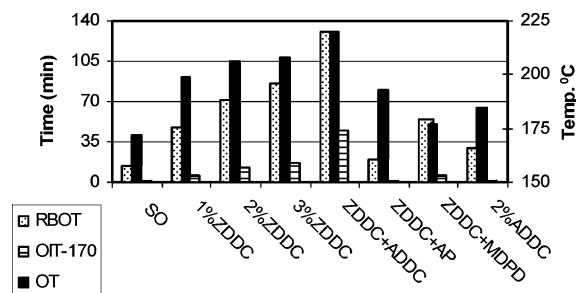


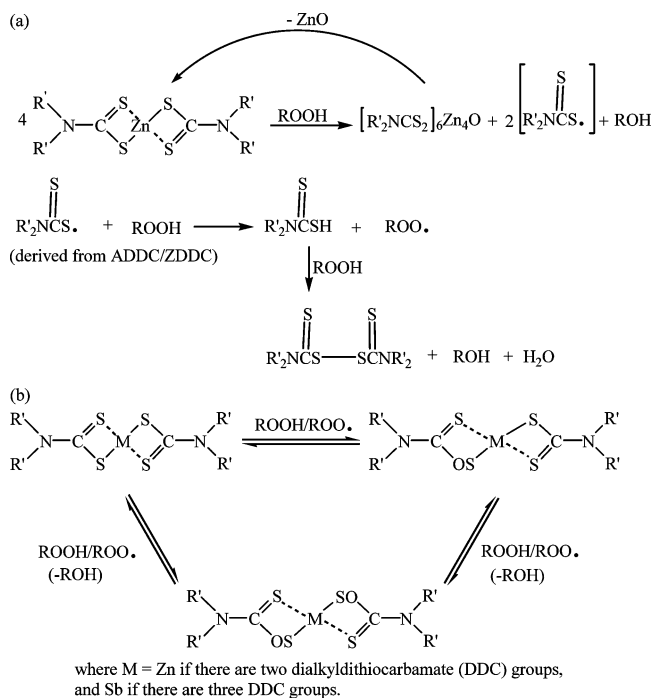
Figure 5. Antioxidant response of additive ZDDC in combination with antiwear additives using PT PDSC, isothermal PDSC (170 °C), and RBOT.

The ADDC or MDPD/APDD combinations were less effective than equivalent quantities of APDD alone. Addition of more diphenylamine (ADPA) also made no change in PDSC oxidation induction times and onset temperatures. The response of different ratios of phenolic/diphenylamine depends on base oils and on phenol structure. In general, as one moves from a 1:1 ratio to either side, the antioxidant efficiency of the mixture decreases.¹⁵ The RBOT results showed no improvement in the antioxidant performance of APDD on addition of antiwear additives. In fact, AP showed pro-oxidant behavior in these test conditions with the RBOT time reduced to 18 min from 38 min for 2% APDD in soybean oil. Possibly under the conditions of the RBOT experiment, antiwear additive AP or the AP peroxide intermediate started decomposing to generate more free radicals that increased the rate of the chain propagation step in oxidation.

Effect of Antiwear Additives on Antioxidant Response of ZDDC. Figure 5 shows the results obtained for various concentrations of ZDDC and its combinations with antiwear additives in soybean oil. Up to a concentration level of 3%, the increase in RBOT time, oxidation induction time, and onset temperature is fairly linear with an increase in ZDDC concentration. This agrees with the linear dependence of ZDDC concentration on the induction period reported in another study.⁵ The strong concentration dependence of ZDDC was attributed to its ability to function both as a radical scavenger and a hydroperoxide decomposer. The mechanism of oxidation inhibition by ZDDC was found to be very effective, which involves complex interactions between alkylperoxy radicals, organic hydroperoxides, and intermediate decomposition products of initial compounds.

The multifunctional nature of ZDDC is well-known, so it will be important to know the effect of other antiwear additives in the system on the antioxidant efficiency of this additive. These antiwear additives were added to 2% ZDDC in soybean oil and their oxidation stability has been evaluated. For ZDDC/AP, and ZDDC/MDPD additive combinations, the RBOT time and oxidation induction time obtained using isothermal PDSC at 170 °C are much less compared to 2% ZDDC in soybean oil, showing that the antiwear additives in these combinations act as pro-oxidants. The RBOT time of 2% ZDDC in soybean oil (71 min) has been reduced to 20 min on addition of amine-phosphate antiwear additive and 55 min with MDPD antiwear additive. The OIT and onset temperature have also been reduced similarly with these combinations. Under the conditions of oxidation tests, i.e., high temperature and pressure, there is a possibility that the phosphate group present in these two antiwear additives is reacting with free radicals and forming some unstable phosphate peroxide intermediates. These unstable intermediates can decompose to generate more radicals that propagate oxidation.

Scheme 2. Recycling Mechanism of Metal Dithiocarbamate through Formation of (a) Dithiocarbamic Acid (Dialkylhydrogendithiocarbamate) and (b) Oxidized Metal Dithiocarbamates



Of the three antiwear additives, only ADDC showed a strong synergistic effect on antioxidant capacity of ZDDC in soybean oil. The onset temperature of 2% ZDDC in soybean oil (207 °C) has increased to 220 °C on addition of 2% ADDC; oxidation induction time has jumped to 45 min from 12 min, while RBOT time doubled to 130 min.

Scant literature information is available to explain the antioxidation synergism of ZDDC with ADDC. Four possible explanations can be considered. The first one for this synergism is the presence of sulfur in metal dithiocarbamates, which has been attributed to the formation of various sulfur oxyacids during hydroperoxide decomposition.^{24,25} These acids participate in the antioxidant mechanism by an acid-catalyzed ionic decomposition of the hydroperoxides.^{26,27} The acid species formed might be dialkylhydrogendithiocarbamate $\text{R}'_2\text{NCS}_2\text{H}$ derived from ZDDC as shown in Scheme 2a. A similar acid species was reported to be formed from zincdialkylthiophosphate,^{26,27} which was a better antioxidant than the parent additive itself.²⁷ Meanwhile, when a strong acid like sulfuric acid is blended into this chemical system, the formation of weaker acidic species like acid dithiocarbamates will result. Thus, the formation of sulfuric acids from ZDDC will lead to production of acid dithiocarbamates. These acid dithiocarbamates formed in mixtures result not only from the ZDDC oxidation process itself but also from the acid-catalyzed decomposition of ADDC. Consequently, the antioxidant capability is increased resulting in synergistic effects for the mixture of ZDDC and ADDC. The formation of such acid dithiocarbamates in the case of ADDC and interfering with oxidation just like ZDDC has been shown by its RBOT time of 30 min compared to the 14 min of soybean oil and its onset temperature of 185 °C compared to the 172 °C of soybean oil.

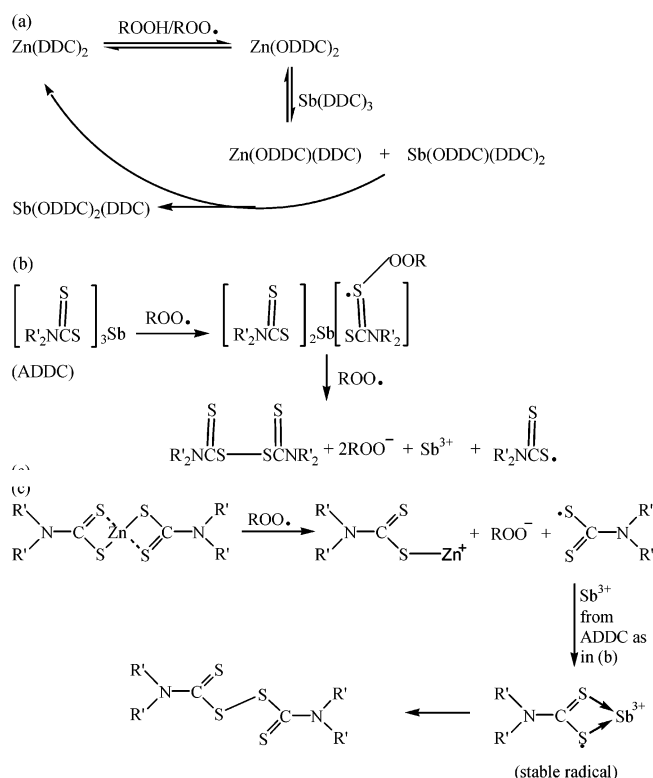
(24) Holcik, J.; Koenig, J. L.; Shelton, J. R. *Polym. Degrad. Stab.* **1983**, *5*, 373.

(25) Sexton, M. D. *J. Chem. Soc., Perkin Trans. II* **1985**, 59.

(26) Bridgewater, A. J.; Dever, J. R.; Sexton, M. D. *J. Chem. Soc., Perkin Trans. II* **1980**, 1006.

(27) Howard, J. A.; Tong, S. B. *Can. J. Chem.* **1980**, *58*, 92.

Scheme 3. Oxidation Inhibition Process of Additive Combination ZDDC/ADDC through (a) Exchange of Ligands and (b and c) Formation of an Sb-Coordinated Intermediate Radical



In the second one, a recycling mechanism shown in Scheme 2b has been suggested for partial recovery of ZDDC or ADDC from their oxidized versions ZODDC or AODDC by peroxy radical scavenging or hydroperoxide decomposition processes, respectively.⁵ The formation of oxidized dithiocarbamate (ZODDC) was identified as main process in the decomposition of *tert*-butylhydroperoxide by ZDDC.⁵ It seems more likely that a reaction sequence from metal dialkyldithiocarbamate via oxidized dialkyldithiocarbamates and a further oxidized metal complex with antioxidant ability and possibly sulfur dioxide accounts for the synergistic antioxidant activity observed. Oxidized metal dithiocarbamates were also reported to have some antioxidant property, although less than unoxidized ones. In other words, the dithiocarbamates and their oxidation products prevent the formation of lubricant radicals and hydroperoxides and increase the antioxidant efficiency of mixtures of metal dithiocarbamates synergistically.

The third one is that the metal ions present in dithiocarbamates also affect the antioxidant efficiency of these additives. ZDDC yields the best results even though there are two dithiocarbamate ligands per molecule compared to three in ADDC. It has been shown by Shea and Stipanovic²⁸ that metal dithiocarbamate appears to exist as ion pairs and their major influences over their reactivity are hard/soft acid/base and solvation interactions. The high antioxidant efficiency of ZDDC may have been regenerated using the dithiocarbamate ligands of ADDC as shown in Scheme 3a. The regeneration of more potent antioxidant ZDDC from a less potent antioxidant like ZODDC formed in Scheme 2b and ADDC may explain their powerful synergistic behavior.

Table 1. Synergism (S) of Additive Combinations in Soybean Oil Using RBOT Results, PDSC Oxidation Induction Times, and Onset Temperatures

| additive combination | RBOT | S-RBOT (%) | S-OT (%) | S-OIT (%) |
|----------------------|------|------------|----------|-----------|
| ZDDC + ADDC | 130 | 159 | 100 | 381 |
| ZDDC + AP | 20 | 11 | 61 | 2 |
| ZDDC + MDPD | 55 | 72 | 14 | 46 |
| ADPA + ADDC | 46 | 200 | 95 | 2440 |
| BHT + ADDC | 53 | 87 | 54 | 207 |
| BHT + ZDDC | 89 | 87 | 63 | 176 |
| APDD + ADDC | 41 | 68 | 53 | 73 |
| APDD + ADPA | 35 | 88 | 76 | 107 |

Finally, as shown in Scheme 3b and c, during peroxide radical scavenging, ZDDC may form dithiocarbamate radicals and antimony of ADDC (Scheme 3b) may form a stable chemical bond with the N or S atoms of these radicals by the coordination effect (Scheme 3c) and prevent the molecule from chemical decomposition due to steric effects. Consequently, this coordinated intermediate radical will be much less sensitive against oxidation and more stable than the original radical. This radical can inhibit the interaction of original radical, so that its efficiency to scavenge radicals was improved effectively. These may be some of the possible reasons that, apart from the added effects of ZDDC and ADDC, they exhibit a strong synergistic effect of their antioxidant efficiency in soybean oil. However, structures of the proposed intermediates from the additives need to be understood for the detailed mechanisms of the synergism between ZDDC and ADDC. A great deal of work is still required to evidence these hypotheses.

Synergism. The synergistic combinations which enhance stabilization at a relatively lower content of each component should be of interest for the formulation of environmentally friendly fluids with diminished additive toxicity. The synergism or lack of synergism of the different additive combinations were calculated and are found in Table 1.

The best RBOT time was obtained with the ZDDC/ADDC combination, although the synergism (S) of the ADPA/ADDC combination was the highest. The synergism of the ZDDC/ADDC combination was calculated in percentage as the increased efficiency of the combination ($\text{RBOT time}_{\text{ZDDC-ADDC}} - \text{RBOT time}_{\text{SO}}$) compared with the computed sum of the single RBOT times minus the RBOT time of the pure oil for each additional component $[(\text{RBOT time}_{\text{ZDDC}} - \text{RBOT time}_{\text{SO}}) + (\text{RBOT time}_{\text{ADDC}} - \text{RBOT time}_{\text{SO}})]$. A synergism exists in the additive combination when the value of S is higher than 100%.

Using PDSC isothermal results, a strong synergism is seen in ADPA/ADDC and ZDDC/ADDC combinations (Table 1). BHT/ADDC and BHT/ZDDC combinations also showed a synergistic effect, but not as strong as that seen with the ZDDC/ADDC combination. The APDD/ADPA combination showed only an added effect, while other combinations resulted in negative effects. In RBOT results, ADPA/ADDC showed the strongest synergism followed by the ZDDC/ADDC combination, similar to PDSC results. All the other combinations yielded no synergistic effect under the RBOT temperature and pressure conditions. The strongest synergistic response of the ADPA/ADDC and ZDDC/ADDC combinations was attributed to the ability of dithiocarbamates to function as hydroperoxide decomposers/metal deactivators/radical scavengers and an additional radical scavenging effect by the amino group of ADPA. ADPA by itself showed no inhibitor effect in soybean oils but in combination with ADDC provided a very high value of synergism. It appears from the ADPA/ADDC combination that the poor inhibition effect of ADPA can be regained by using it with some other additives like dithiocarbamates. The effect of

(28) Shea, T. M.; Stipanovic, A. J. *Tribol. Lett.* **2002**, 12 (1), 13–22.

(29) *Lubricants Industry Sourcebook 2004–2005 – A Supplement to Lubes 'n' Greases*; Persaud, M., Ed.; LNG Publishing Company, Inc.: Falls Church, VA; p 4.

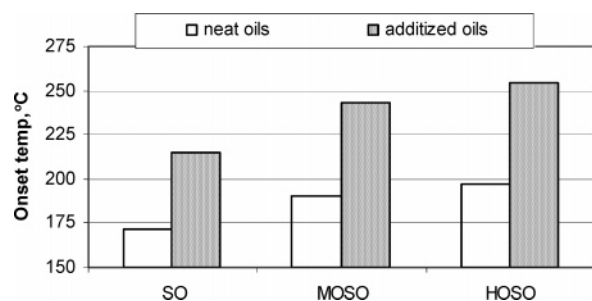


Figure 6. PT PDSC results for ZDDC/ADDC combinations in various base oils.

various antioxidant mixtures such as ADPA/BHT and ADPA/ZDDC are already reported in the literature.⁵ BHT/ADPA combinations resulted in added or slightly negative effects, while the ADPA/ZDDC combination resulted in a synergism value of 165. On the basis of these literature values, a similar or higher value can be expected for the ADPA/ZDDC combination under experimental conditions described in the present work. The ADPA/ADDC combination thus provided an RBOT time of only 46 min, while the ZDDC/ADDC combination resulted in an RBOT time of 130 min in soybean oil. Overall the ZDDC/ADDC additive combination was found to be the best one in soybean oil increasing its oxidation stability almost 10-fold.

Base Oil Effects on ZDDC/ADDC Synergism. The effect of the base oil type on the PDSC onset temperature of oils blended with ZDDC/ADDC is shown in Figure 6. The main difference in these oils is in their oleic acid content and thus polyunsaturation. The oleic acid content in regular soybean oil (SO) is 24.2%, mid-oleic soybean oil (MOSO) has 60.7%, and high-oleic soybean oil (HOSO) has 86.8%. The variation of additives response in base oils is considerably high. While the difference in oxidation onset temperatures of MOSO and SO is 18 and that of HOSO and SO is 25, a significantly stronger antioxidant response in MOSO and HOSO is observed. On addition of 2% ZDDC and 2% ADDC to these oil samples, the

OT difference between additized MOSO and SO has increased to 28, while that of additized HOSO and SO jumped to 39.

The RBOT time of SO, MOSO, and HOSO without additives is 14 min. With the addition of the ZDDC/ADDC additive combination, the RBOT time of soybean oil has improved to 130 min and that mid-oleic soybean oil has increased to 284 min, while that of additized high-oleic soybean oil is amplified to 469 min. This shows that there is significantly stronger response to this additive combination in HOSO compared to SO.

The following conclusions can be drawn from the PDSC and RBOT results obtained for additives in vegetable oils.

(1) Among the antioxidants, ZDDC exhibited the best antioxidant activity followed by BHT and APDD, while the antioxidant performance of ADPA was found to be inhibited in soybean oil.

(2) All antioxidants showed improved performance with antiwear additive ADDC compared to molybdenum phosphorodithioate, while an ashless antiwear additive containing amine-phosphate resulted in poorer antioxidant performance. The additives ADDC and MDPD demonstrated a multifunctional nature by showing antioxidant behavior apart from their normal function as friction reducers.

(3) In vegetable oils, the ZDDC and ADDC combination exhibited a strong synergistic antioxidant effect.

(4) The additive combination ZDDC/ADDC showed a significantly stronger antioxidant response in vegetable oils with increased oleic acid content or decreased polyunsaturation.

Additive and base oil selection contributes profoundly to improved oxidation stabilities of vegetable oils at elevated temperatures. The availability of reasonably priced high-oleic vegetable oils along with the best additive combinations will pave the way for a major utilization of vegetable oils in industrial and automotive applications.

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